

CATALYTIC HYDROGENATION OF CO₂ INTO HYDROCARBONS:
SUPPORT EFFECTS ON Fe AND Fe-K CATALYSTS.

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INTRODUCTION

Since accumulation of carbon dioxide in the atmosphere is now regarded as one of the major reasons of the Global Warming, interest in the reutilization of carbon dioxide is on the increase [1-10]. It is desirable for the reutilization of carbon dioxide to develop the technology for the hydrogenation of carbon dioxide to valuable materials such as light olefins or liquid hydrocarbons.

However, relatively little attention has been paid so far to the catalytic hydrogenation of carbon dioxide while carbon monoxide hydrogenation has been extensively investigated with the purpose of utilization of coal as a carbon source. In previous studies [11-16], iron-based catalysts, which are originally used in the Fischer-Tropsch (F-T) reaction, have been applied to the hydrogenation of carbon dioxide to hydrocarbons. According to the results, however, it seems that those catalysts are not satisfactory because they give only small yield of C₁ hydrocarbons with the significant production of carbon monoxide and methane. It seems that the different catalytic properties are required for the hydrogenation of carbon dioxide because the chemical properties of carbon dioxide is different from carbon monoxide. Therefore, more systematic work is necessitated in order to develop suitable catalysts for the production of light olefins or liquid hydrocarbons from carbon dioxide hydrogenation.

While varying potassium content in the alumina-supported Fe-K catalysts, we found that the catalysts having high K content (K/Fe atomic ratio = 0.5-1.0) give considerably high conversion and selectivity to C₂ hydrocarbons and light olefins [17]. In the present work, we have investigated the support effects on Fe and Fe-K catalysts with the hydrogenation of CO₂.

EXPERIMENTAL

Silica gel, γ -alumina and titania (anatase) were used as the support materials. The BET surface areas, pore volumes and average pore diameters of support materials were determined by N₂ adsorption at -196°C adsorption using a volumetric apparatus (Micromeritics ASAP 2400). Characteristics of support materials are listed in Table 1.

Supported iron oxide catalysts with an iron loading of 20%(w/w) were prepared by impregnating silica gel, γ -alumina (Strem, 157m²/g) and titania (anatase) with an aqueous solution of Fe(NO₃)₃·9H₂O. To prepare supported iron-potassium catalysts with K/Fe molar ratio = 0.5), an adequate amount of K₂CO₃ was added into the aqueous solution of Fe(NO₃)₃·9H₂O before impregnation. After the impregnation, the catalyst samples were dried at 383 K for 24 hr and calcined in air at 773 K overnight.

The temperature programmed decarburization was performed with the catalysts reacted with a mixture gas of carbon dioxide and hydrogen at 573 K and 1 atm for 30 min followed by cooling down to room temperature with purging helium. The gas was changed to hydrogen and the temperature of catalyst bed was increased to 923 K with the ramp of 5 K/min. The evolved product was mainly methane and it was analyzed continuously by a flame ionization detector, which gave the temperature programmed decarburization profile.

The catalytic hydrogenation of carbon dioxide was performed in a

continuous fixed bed reactor. The catalyst was reduced in a flow of hydrogen at 723 K for 20-24 hr. After the reduction, the catalyst was brought to the reaction temperature and then the feed changed to the mixture gas of carbon dioxide and hydrogen. Space velocity was 1900 ml/g-cat.h. The products were analyzed by a gas chromatograph (Chrompack CP 9001) equipped with thermal conductivity and flame ionization detectors. Carbon monoxide, carbon dioxide and water were analyzed on a Porapak Q column and the hydrocarbons on a Poraplot Q capillary column. The experimental data were taken after 24 hr of the reaction.

RESULTS AND DISCUSSION

In the temperature programmed decarburization, the surface carbides are investigated by the temperature programmed decarburization, which shows the relative amount and stability of surface carbon species formed during the reaction.

Figure 1 shows the decarburization profile of the supported iron catalysts after treatment at the reaction condition for 30 min. The decarburization profile of the Fe/silica catalyst shows a single peak with a maximum peak temperature of 690 K. However, with the γ -alumina supported catalyst, the profile shows two peaks (685 K and 725 K), which indicates the presence of two types of carbides. The peak appearing at higher temperature (725 K) represents that more stabilized carbide is formed during the reaction on Fe/ γ -alumina. With the titania (anatase) supported catalyst, the profile shows two peaks also, but high temperature shift. The result of the high temperature shift reveals that supporting on titania (anatase) increases the stability of surface carbides on the catalyst. It seems that interaction between iron and supports exists with Fe/ γ -Al₂O₃ and Fe/TiO₂, as compared to the silica supported catalyst. It is likely that the enhancement of carbide stabilization is due to the metal-support interaction.

The hydrogenation of carbon dioxide over supported iron catalysts produces both carbon monoxide and hydrocarbons, and the influence of support on the activity and selectivity of the reaction was examined.

Table 2 shows the results of CO₂ hydrogenation on supported Fe catalysts at 573 K and 10 atm. The conversion data reflect that activities for CO₂ hydrogenation decrease in order Fe/TiO₂, Fe/ γ -Al₂O₃, Fe/SiO₂. This apparently indicates that the catalytic activity is not dependent on the surface area of support material. From the selectivity data, it will be seen that the catalysts Fe/TiO₂ and Fe/ γ -Al₂O₃ show much higher selectivity for hydrocarbons than Fe/SiO₂. Furthermore, Fe/TiO₂ and Fe/ γ -Al₂O₃ give higher selectivity for C₂ hydrocarbons as compared to the silica supported catalyst. Especially, Fe/TiO₂ shows the highest selectivity for C₂ hydrocarbons. These results also indicate that the metal-support interaction exists with Fe/ γ -Al₂O₃ and Fe/TiO₂. The high product selectivity for long-chain hydrocarbons with Fe/TiO₂ might be correlated with the results of decarburization which show that the carbides formed during the reaction are more stabilized by titania (anatase) support. It is reported that iron carbides are responsible for the formation of long-chain hydrocarbons in CO₂ hydrogenation [16].

We found that the promotion of Fe/Al₂O₃ with high K content gives the improvement in the catalytic performance for CO₂ hydrogenation to hydrocarbons [17]. The influence of support on the catalytic performance of Fe-K (K/Fe = 0.5) was examined also. Table 3 shows the results of CO₂ hydrogenation on supported Fe-K catalysts at 573 K and 10 atm. With silica and titania supports the addition of potassium decreases the catalytic activity and selectivity for hydrocarbons. In contrast, with γ -alumina support, the addition of potassium increases the catalytic activity. However, with all catalysts, the addition of potassium increases the selectivity for C₂ hydrocarbons and light olefins. It should

be noted that the combination of Fe, K and γ -alumina makes the catalyst bearing considerably high activity and selectivity. It seems that γ -alumina is not only a support but a kind of promotor in Fe-K/ γ -Al₂O₃.

SUMMARY

The effects of support on CO₂ hydrogenation into hydrocarbons over Fe and Fe-K catalysts have been investigated. The catalysts were prepared by impregnation using silica gel, γ -alumina and titania (anatase) as supports. The results of temperature programmed decarburization showed that weak interaction between iron and support exists with Fe/ γ -Al₂O₃ and strong interaction with Fe/TiO₂. The titania-supported iron catalyst gave much higher conversion and selectivity towards C₂ hydrocarbons than silica-supported iron catalysts. It is likely that the high catalytic activity and selectivity of Fe/TiO₂ are due to metal-support interaction. While potassium was being introduced into the catalysts as a promotor, it was found that potassium increased the selectivity for C₂ hydrocarbons and olefins on all supports, but increased the catalytic activity on only γ -alumina. The combination of Fe, K and γ -Al₂O₃ makes the catalyst highly active and selective for CO₂ hydrogenation to C₂ hydrocarbons and light olefins. It seems that γ -alumina functions as a promotor in Fe-K/ γ -Al₂O₃.

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Table 1. Characteristics of supports

Support material	BET surface area (m ² /g)	Pore volume (cc/g)	Average pore diameter (Å)
SiO ₂	462	0.731	63
Al ₂ O ₃	157	0.407	104
TiO ₂	10	0.030	118

Table 2. Effects of support on CO₂ hydrogenation performance of Fe catalysts^a

Catalyst	Conv. (%)	Selectivity (C %)		Distribution of HC (C %)			O/P ratio in C ₂₋₄
		CO	HC	C ₁	C ₂₋₄	C ₅₊	
Fe/SiO ₂	22.1	61.6	38.4	59.7	34.2	6.1	0.02
Fe/Al ₂ O ₃	43.9	4.7	95.3	27.1	54.2	18.7	0.01
Fe/TiO ₂	51.3	5.2	94.8	25.2	54.3	20.5	0.05

^aCO₂ hydrogenation at 1900 ml/g/h, 573 K and 10 atmTable 3. Effects of support on CO₂ hydrogenation performance of Fe-K (K/Fe = 0.5 atom ratio) catalysts^a

Catalyst	Conv. (%)	Selectivity (C %)		Distribution of HC (C %)			O/P ratio in C ₂₋₄
		CO	HC	C ₁	C ₂₋₄	C ₅₊	
Fe-K/SiO ₂	14.2	62.6	37.4	14.1	59.0	26.9	3.20
Fe-K/Al ₂ O ₃	57.7	12.7	87.4	7.1	48.2	44.7	7.11
Fe-K/TiO ₂	8.4	58.1	41.9	16.6	54.3	30.4	1.01

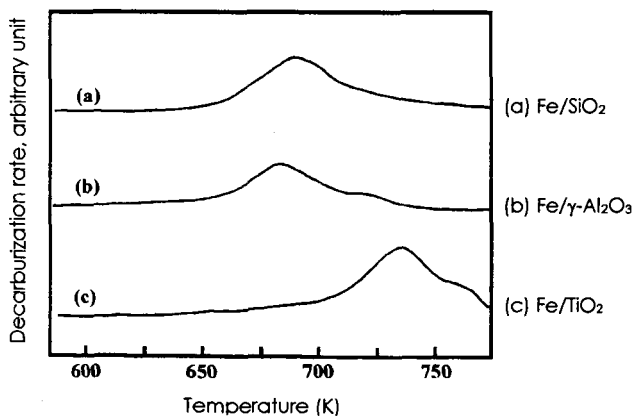
^aCO₂ hydrogenation at 1900 ml/g/h, 573 K and 10 atm

Figure 1. Temperature programmed decarburization of carbides on the catalyst surface.